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DEVELOPMENTS IN USSR WORK ON HYDROCARBONS

[Comment: The current development of a petrochemical trend in USSR petroleum technology has already been noted (cf. 00-W-31428 and "The Petrochemical Trend in the Petroleum Conversion Industry" by S. K. Makarov, D. I. Orochko, L. A. Potolovskiy, and D. Kh. Teregulov, *Neftyanaya Promyshlennost'*, Vol 33, No 2, Moscow, Feb 1955, pp 67-71). On the occasion of the 200th anniversary of Moscow University, present and past research on hydrocarbons at that university has been reviewed rather extensively in a number of publications. These reviews emphasize the use of petroleum hydrocarbons and natural gas as crude materials for the chemical industry. In discussing the work on the kinetics of the oxidation of hydrocarbons and chemical kinetics in general conducted by N. M. Emanuel' at Moscow University (see below), R. Ya. Levina stresses the importance of this work from the standpoint of the production of industrial chemicals derived from hydrocarbons and of the savings which can be achieved by increasing the stability of lubricating oils to oxidation.

Academician A. N. Nesmeyanov, president of the Academy of Sciences USSR, states that control of the formation of radicals and of chain reactions which may be achieved on the basis of studies in the field of chemical kinetics is of importance from the chemical standpoint mainly in that it furnishes a tool by means of which intermediate oxidation products of industrial significance such as formaldehyde can be produced, and polymerizations leading to synthetic resins, elastomers, and other products, can be stopped at the desired point. He also states, however, that the study of chain reactions, particularly branched chain reactions, is of importance for still another reason, i.e., because results obtained in this field enable one to understand processes occurring in

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combustion and explosions and to control atomic explosions (A. N. Nesmeyanov, "Future Developments in USSR Science," Pravda, Vol 44, No 365, Moscow, 31 Dec 1955; cf. 00-W-31678).

Emanuel' himself, in reviewing current USSR work on reaction kinetics, deplored the fact that decreased attention is being paid in this work to the kinetics of combustion and explosions and problems connected with flame propagation (see section on the oxidation of hydrocarbons in the text of the report below). Reduced attention to work of this type may perhaps be explained by the trend mentioned above: there is an increased tendency to utilize hydrocarbons as crude material for the chemical industry and less emphasis on their use as fuels which are subjected to destructive oxidation. Furthermore, the combustion of fuels of the medium boiling range which are used in reaction motors and diesels requires maintenance of less rigid conditions than the combustion of light fuels in conventional gasoline-driven engines of the reciprocating type; hence decreased attention is being paid to kinetics of combustion, although a considerable amount of work on chain reactions and reaction kinetics in general is apparently being done.]

Work on Hydrocarbons at Moscow University

Some recent advances in the chemistry of hydrocarbons in the USSR, and the background of these advances with particular attention to work done at the Moscow State University imeni M. V. Lomonosov, are outlined below.

N. D. Zelinskiy, and after him A. F. Frost, demonstrated that petroleum is of organic origin: they established that the most diverse materials of animal and plant origin can be converted into hydrocarbon mixtures similar to petroleum when these materials are acted upon by aluminum chloride or converted in contact with natural or artificial clays acting as catalysts. Crude petroleum serves as a source of hydrocarbons for fuels and for the chemical industry. The necessity of developing methods for the use of gaseous hydrocarbons derived from natural gas and petroleum gas as initial materials in the synthesis of rubber, synthetic fibers, detergents, and other products has been pointed out by the July 1955 Plenary Session of the Central Committee CPSU.

Moscow State University has placed particular emphasis on research in hydrocarbon chemistry since the 1880s, when V. V. Markovnikov worked in this field in connection with the exploitation of the Caucasian oil fields. Work in this field has been especially productive of practically applicable results during the period [up to 1938] when N. D. Zelinskiy [Markovnikov's successor as head of the Chair of Organic Chemistry at Moscow University] was in charge of it. By using the reaction of the catalytic dehydrogenation of naphthenes to aromatics discovered by Zelinskiy, the reaction of the aromatization of paraffins over a platinum catalyst according to a procedure discovered by B. A. Kazanskiy and A. F. Plate, and the catalytic conversion of cyclopentanes into branched paraffins according to the method of Zelinskiy and Kazanskiy, one can, if the need arises, achieve complete aromatization of the total amount of hydrocarbons contained in the gasoline and kerosene fractions of crude oil. Zelinskiy and Kazanskiy's method involves fission of the ring under the action of hydrogen during a conversion of the cyclopentanes with the use of a platinum catalyst.

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Work by Zelinskiy and A. A. Balandin has made feasible the production of synthetic rubber from petroleum raw materials. These investigators have developed a method for the conversion into butadiene of the butane and butene which are contained in considerable quantities in gases evolved during the thermal cracking of petroleum. Under the action of metal oxide catalysts, these two gaseous hydrocarbons are converted into butadiene at a temperature of about 500°. Because production of synthetic rubber from petroleum raw materials has been made possible in this manner, this production no longer depends on a supply of ethyl alcohol and the conversion of alcohol by S. V. Lebedev's method.

In recent years Profs N. I. Shuykin, R. Ya. Levina and M. B. Turova, and Docent S. I. Khromov (Moscow University) have investigated many other catalytic reactions of hydrocarbons from the standpoint of their application in the petroleum industry and in the conversion of products derived from petroleum. At the Chair of Physical Chemistry, Profs A. V. Frost and K. V. Topchiyeva have subjected to investigation the mechanism and rate of various transformations of petroleum hydrocarbons under the effect of aluminosilicate catalysts, which are widely used in industrial processes of petroleum conversion.

On the basis of data relating to the catalytic conversion of hydrocarbons, A. A. Balandin has proposed the so-called multiplet theory of catalysis, which postulates that the reacting molecules and the catalyst must bear a definite relationship to each other both structurally and thermodynamically. According to Balandin's theory, molecules as a rule react after coming into contact with a whole group of atoms of the catalyst (i.e., a multiplet) rather than with a single atom.⁽¹⁾

The multiplet theory postulates that active centers composed of groups of atoms are effective on the surface of the catalyst. The catalytic activity of these groups of atoms constituting the multiplets is based on a correspondence between the geometric arrangement of groups contained in the molecule of the substance being converted and the geometric configuration of the multiplets. It is also determined by certain requirements with regard to the energy balance. According to this theory, a heterogeneous catalytic reaction proceeds over the formation of an unstable complex between the reacting molecules and the active centers of the catalyst. The complexes are formed only when there is direct contact, i.e., the chemical valency forces have a small radius of activity. Those atoms of the reacting molecules among which a redistribution of valency bonds takes place come into contact with the active centers. It is assumed that the reaction takes place in a monolayer, i.e., on the surface of the catalyst.

N. I. Kobozev's theory of active ensembles resembles Balandin's theory in that the active center of the catalyst is assumed to have a definite structure corresponding to the distribution of atoms in the reacting molecules. The surface of the catalyst is assumed to have a compartmentalized structure: it consists of individual closed regions which are separated from each other by structural and potential barriers beyond which the atoms of the catalyst cannot migrate. If an ensemble consisting of n atoms of the catalyst disposed on the surface of one of the regions or cells is active, the maximum catalytic activity will be attained when a certain optimum concentration of catalyst atoms on the surface has been established; an increase or a reduction of the concentration will destroy the ensembles consisting of n atoms. Kobozev believes that by determining the dependence of the relative specific activity of the catalyst on the degree of filling of the surface, one can, if the surface of the carrier is known, arrive on the basis of his theory at conclusions not only in regard to the number of atoms forming an active center, but also in regard to the structure of the catalyst.

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Lately the radical-chain theory of heterogeneous catalysis has received some acceptance. This theory is being elaborated by F. P. Vol'kenshteyn, N. N. Semenov, and V. V. Voevodskiy. According to the radical-chain theory, some free valencies are present on the surface of the catalyst. These valencies are formed as a result of the excitation of electrons of the solid catalyst by heat motion. Molecules which are saturated with respect to their valency bonds, on reacting with the free valencies of the catalyst surface, form radicals. These radicals may either penetrate into the space above the catalyst, inducing radical or chain reactions there, or initiate chain reactions that proceed on the catalyst.(2)

In addition to doing work on problems of catalysis, the chemical research workers at Moscow University are conducting extensive investigations on the synthesis of hydrocarbons. R. Ya. Levina and her collaborators have developed new methods for the synthesis of many straight-chain and cyclic hydrocarbons the structure of which was formerly not known (1).

Levina established the fact that all unsaturated hydrocarbons have one property in common, i.e., that of isomerizing at a relatively low temperature (260°) in the presence of metal oxides. In developing new methods for the synthesis of hydrocarbons, she utilized the high reactivity of unsaturated hydrocarbons of the butadiene and cyclodiene series (3).

The availability of convenient methods of synthesis facilitates work on important problems such as the dependence between the structure of hydrocarbons and their properties as motor fuels and lubricants, determination of the structure of individual components of crude petroleum by comparing them with synthetic compounds, etc.

Work on the qualitative and quantitative analysis of hydrocarbon mixtures (gasolines, kerosenes, etc.) by determining their Raman spectra is being conducted by Prof V. M. Tatevskiy and members of his group. In the course of this work, the characteristics of Raman spectra of hydrocarbons of many types have been investigated and relationships established between the structure of these hydrocarbons and their spectra.

The conversion of hydrocarbons into other organic compounds is also being subjected to extensive investigation. At the Laboratory of Organic Synthesis, which is directed by Levina, a reaction has been developed by means of which cyclopropanes can be converted into compounds that contain an atom of mercury and a carbinol group. These compounds exhibit antibacterial activity.

At the Laboratory of Gas Electrochemistry the problem of converting methane into acetylene has been solved. Profs N. I. Kobozev and S. S. Vasil'yev have worked on this method.

At the Chair of Chemical Kinetics, Prof N. M. Emanuel' is conducting investigations on reaction velocities and the mechanism of the oxidation of hydrocarbons. By oxidizing hydrocarbons, substances which are of importance from the economic standpoint (carboxylic acids, alcohols, etc.) can be obtained. Problems pertaining to the oxidation of hydrocarbons are also of importance from another standpoint, i.e., the stability of lubricating oils to oxidation. If the stability of lubricants to the oxygen of the air can be increased, a considerable economic gain will result.

Prof P. P. Borisov and Docent M. S. Eventova have investigated the oxidation of specially synthesized hydrocarbons of types which enter into the composition of lubricating oils and established the dependence between the structure of these hydrocarbons and their stability to oxidation.

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A brief review of the work of the Chemical Faculty of Moscow State University shows that this work deals with all the essential subdivisions of hydrocarbon chemistry which are of importance for advancing the development of branches of industrial technology that depend on the use of hydrocarbons as crude material.(1)

Catalytic Cracking

The majority of new processes applied in the USSR petroleum conversion industry are based on work done by chemists. The discovery of the cracking of hydrocarbons by V. G. Shukov in the 1890s led to a reorientation of the world petroleum industry and was the most important factor which transformed petroleum conversion into a branch of the chemical industry. An improvement in the yield of gasoline and in the antiknock properties of the gasoline was achieved not only by perfecting the technology of thermal cracking, but also by developing new methods of catalytic cracking. As far as catalytic cracking is concerned, one must mention S. V. Lebedev's work on the catalytic polymerization and depolymerization of alkenes in the presence of aluminosilicate catalysts. Aluminosilicate catalysts, the catalytic properties of which were originally established by L. G. Gurvich, are at present extensively applied to catalytic cracking.

By 1918 N. D. Zelinskiy had developed a method for the catalytic cracking of mazut with aluminum chloride at 150-200° in which a yield of gasoline exceeding 60% was obtained. The first experiments on the use of aluminum chloride for this purpose were carried out by G. G. Gustavson [a Russian chemist who was active around 1870.](4)

The first USSR cracking installation was built in 1923 at Baku by V. G. Shukov and M. A. Kapelyushnikov.(5) In the development of petroleum chemistry and technology, work done by Zelinskiy and S. S. Nametkin was of fundamental importance. One must also mention in this connection work done by TsIATIM [Central Scientific Research Institute of Aviation Fuels and Oils], Groznyi Scientific Research Petroleum Institute], ANII [Azerbaijani Scientific Research Petroleum Institute], and the petroleum institutes of the Academy of Sciences USSR and the Academy of Sciences Azerbaijan SSR.

Important investigations pertaining to petroleum technology have been carried out under the Soviet regime by A. V. Frost, D. I. Orochko, B. K. Amerik, V. S. Gutrya, and others.

Orochko, G. K. Boreskov, and M. F. Nagiyev have done theoretical work which has a bearing on petroleum technology: Orochko worked on hydrogenation equipment, Boreskov on the determination of the optimum temperature field of the reaction zone, and Nagiyev on processes carried out in stages in such a manner that the products are withdrawn between the stages.

High-capacity units for the conversion of petroleum operate continuously. By using the principle of recirculation, a degree of conversion approaching 100% is achieved in them. Notwithstanding the fact that this principle had been applied for a long time, no general theory of recirculation processes existed. Nagiyev developed such a theory recently (4).

In view of the fact that industrial catalytic cracking is carried out with the aid of alumina-silica catalysts, the chemistry of contemporary cracking is mainly one of the transformations of hydrocarbons under the effect of active aluminosilicates.

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The polymerizing action of natural aluminosilicates has been investigated in detail by S. V. Lebedev and members of his group. The work in question has shown that catalytic depolymerization of alkenes in the presence of aluminosilicates proceeds at a higher velocity and at lower temperatures than thermal cracking.

Lebedev and Ye. P. Filonenko determined that the polymerization products of nonsymmetric alkenes (i.e., of compounds which are capable of polymerization at room temperature) depolymerize when heated in the presence of the same alumina-silica catalyst which had been used originally in polymerization. In work on the decomposition of diamylenes in the presence of aluminosilicates that had been done by Lebedev, it was shown that the decomposition of the hydrocarbons begins at 65-70°. The rate of decomposition markedly increases at 90° and reaches a maximum at 165-170°. The products of the decomposition of diamylenes contain not only alkenes but also saturated hydrocarbons. A more detailed investigation of the depolymerization of isobutene polymers has shown that triisobutene is readily depolymerized at 175-200° in the presence of an alumina-silica catalyst and that intensive cracking begins at 260°.

It has thus been established that scission of hydrocarbons takes place under the influence of alumina-silica catalysts after a very short time of contact of the hydrocarbons with the catalysts. It was found in later work when alkene vapors are brought into contact with alumina-silica catalysts at temperatures in the vicinity of 250°, a complex process takes place during which reactions of scission, dehydrogenation, decomposition into the elements, and polymerization occur simultaneously.

Lebedev experimentally demonstrated that alkanes may form from the corresponding alkenes and determined that simultaneously with the hydrogenation, dehydrogenation and then polymerization of the products of dehydrogenation takes place. These phenomena have been subsequently subjected to a thorough and many-sided investigation by A. V. Frost and his collaborators.

In work done by Lebedev et al., it was repeatedly noted that isomerization of alkenes and alkadienes occurs in the presence of alumina-silica catalysts, and that this isomerization consists in a transformation of the unsymmetric alkene structure into a symmetric one. This work was continued by Ya. M. Slobodin, who showed that methylallene is isomerized into butadiene at 230-275° in the presence of aluminosilicates, while unsymmetric dimethylallene is isomerized into isoprene. Ye. K. Serebrynkova and A. V. Frost established the fact that under the effect of activated clays normal butane is transformed into isobutene. Using an alumina-silica catalyst, A. V. Frost and Ye. K. Remiz hydrogenated propene. They found that the catalyst exerted a very strong hydrogenating action.

The catalytic transformations of hydrocarbons (cracking, alkylation, alkylation conjugated with dealkylation, etc.) are being subjected to systematic investigation by A. V. Topchiyev and Ya. M. Pauskin, A. D. Petrov and N. I. Shuykin, Yu. G. Mamedaliyev, K. V. Topchiyeva, and G. M. Panchenkov. Extensive investigations in this field have been carried out by N. D. Zelinskiy and members of his school, particularly B. A. Kazanskiy, S. R. Sergiyenko, and A. P. Piate. The theoretical postulates formulated by these workers are of great importance for understanding the mechanism of catalytic transformations of hydrocarbons.

D. I. Orochko, A. V. Frost, M. F. Nagiyev, and Z. G. Petrova investigated the catalytic cracking and kinetics of decomposition of cetane as well as of narrow distillation fractions of petroleum within a wide range of temperatures and degrees of conversion.

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Extensive investigations on the catalytic cracking of individual hydrocarbons and petroleum fractions under pressure have been carried out at the Petroleum Institute, Academy of Sciences USSR, under the direction of K. P. Lavrovskiy.

As far as the activity of alumina-silica catalysts is concerned, V. I. Vernadskiy pointed out that the aluminosilicate group is the bearer of this activity. Original and valuable results on the mechanism of the action of these catalysts have been obtained by K. V. Topchieyeva and G. M. Panchenkov. (6)

Results published in 1954 indicate that aluminosilicate cracking catalysts, which are typical acid catalysts, have the properties of semiconductors. Their electrical conductivity changes sharply during cracking. The transition of electrons may precede or accompany the transition of protons. Both the facility with which the transition processes take place and the effect of these processes on the reactivity of molecules of the carbonium and carbanium types are determined in the final end by the electronic structure of the molecules. Such chemical bonds as the hydrogen bond, which evidently plays a prominent role in acid-alkali catalysis, are distinguished primarily by the character of the electron bonds which form them. One may conclude from this that electron phenomena must also play an important role in acid-alkali catalysis. The investigation of the latter from this point of view appears to be promising (7)

Polymerization

Notwithstanding the industrial application since 1939-1940 of the process of alkylation of isobutane with olefins, polymerization has not lost its importance in the petroleum industry. The use of polymerization processes in the industry is not restricted to the synthesis of motor fuels. To give an example, the polymerization of propane yields dodecylene, an olefin which is used for the synthesis of alkyl-aromatic compounds from which synthetic detergents are derived.

By the low-temperature polymerization of isobutene additives to lubricating oils are obtained, while the copolymerization of isobutene with a small quantity of butadiene results in special grades of synthetic rubber which are resistant to the action of chemical agents.

By polymerizing ethylene and other olefins with the aid of aluminum chloride, lubricating oils which have very advantageous characteristics are obtained.

Phosphoric acid as a polymerization catalyst has been subjected to thorough study by Russian investigators.

In 1932 S. S. Nametkin, together with M. G. Rudenko and A. N. Abakumovskaya, discovered a new type of transformation of olefinic hydrocarbons, i.e., the reaction of polymerization accompanied by hydrogenation and dehydrogenation. A study of this reaction has made it possible to explain the changes which take place in the process of the polymerization of olefins and lead as a result of the redistribution of hydrogen to the formation of paraffinic, naphthenic, and aromatic hydrocarbons in addition to that of olefins.

B. A. Kazanskiy and M. I. Rozengart and also A. D. Petrov and his collaborators (A. P. Meshcheryakov and L. I. Antsus) have made a considerable contribution to the knowledge of polymerization and of polymerization products. Kazanskiy investigated the polymerization of olefins in the presence of silicate catalysts ~~and of phosphoric acid. He also studied the mechanism of~~

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constitution of the polymerization products and elucidated the nature of the catalytic action of aluminosilicates, which amounts to ordinary acid catalysis. The work of A. D. Petrov on the chemical structure of some products of the polymerization of olefins is of outstanding importance.

A. V. Topchichev and his collaborators (B. M. Tumerman, T. P. Vishnyakova, V. A. Andronov, and others) investigated the polymerization of olefins in the presence of derivatives of boron fluoride as well as the constitution of the products which are obtained when boron fluoride catalysts are used. In these investigations it was shown that the ether-boron fluoride complex and the compound of boron fluoride with phosphoric acid are of the greatest interest as polymerization catalysts. Their action was found to be analogous to that of ordinary acid catalysts.

R. D. Obolentsev et al. have carried out a great number of investigations on the polymerization, depolymerization, isomerization, and other transformations of hydrocarbons.

N. N. Semenov advanced the productive hypothesis in regard to the occurrence of ionic heterogeneous catalysis, an idea which was confirmed experimentally in work done by N. M. Chirikov and others. If Semenov's hypothesis is valid, catalysis is brought about by ions adsorbed on the surface of a carrier which has a high specific surface, this being a set of conditions which is typical for carriers in the presence of phosphoric acid and for silicate catalysts activated with acids. The chain theory of chemical reactions, which has been developed by Semenov, contributes to an understanding of polymerization processes, which proceed by a chain mechanism.

Yu. G. Mamedaliyev in a series of investigations investigated and developed methods of the conversion of hydrocarbon gases into motor fuels by polymerization and alkylation, thus contributing to progress in this field.

Lately Ya. T. Eydus has published several interesting review articles on the polymerization of olefins, in which an extensive bibliography on the subject is given.

Although production of motor fuels by polymerizing gaseous olefins with the aid of phosphoric acid has been carried out in the petroleum industry for nearly 20 years, the USSR literature hitherto paid only very slight attention to a scientific and technical analysis of processes of olefin polymerization, the theory and kinetics of polymerization with the aid of phosphoric acid catalysts, and other, related problems. The book Kataliticheskaya Polimerizatsiya Olefinov V Motornoye Toplivo by Ya. M. Paushkin attempts to eliminate this blank by reviewing the principal work on the polymerization of olefins into motor fuels and light polymers, the problems of the catalytic conversion of olefins which are connected with this work, the chemical constitution of the products of polymerization, and the fundamentals of the theory of polymerization. The polymerization of isobutene into polyisobutene is considered in connection with a discussion of the utilization of cracking gases. (8)

The polymerization of olefins at atmospheric pressure is thermodynamically feasible at atmospheric pressure both at low temperatures (minus 100° to 0°) and medium temperatures (0° to plus 100°). The conversion takes place if a catalyst is present and good yields are obtained.

The following polymerization catalysts are used: (a) acids: sulfuric, phosphoric, and hydrogen fluoride; (b) halides: aluminum chloride, boron fluoride, and zinc chloride; (c) alumina-silica catalysts and other silicate catalysts.

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According to the views held at present, the mechanism of the action of catalysts which polymerize olefins is based on ionic catalysis. The acids release ions which are assumed to initiate the reaction. Active acids may form when the halides functioning as catalysts combine with traces of moisture or with hydrogen halides. The aluminosilicates also have acidic properties (9)

Oxidation of Hydrocarbons

N. M. Emanuel' subjected to investigation the action of inhibitors and of positive catalysts on chain reactions. On a number of examples of chain reactions, this investigator showed that there is a succession of macroscopic stages separate in time, and that each of these stages is capable of proceeding by a chain reaction. He expressed the opinion that positive catalysts exert an effect on the total process by stimulating the initial macroscopic stage and that the products of this reaction stage then give rise to subsequent stages. The correctness of this conclusion was illustrated on examples (cf. also Z. K. Mayzus, N. M. Emanuel', *Doklady Akademii Nauk SSSR*, Vol 37, 1952, pp 241, 437, 501). On the other hand, the negative catalysts or inhibitors suppress the total process by inhibiting the initial reaction which gives rise to subsequent stages. For this reason, inhibitors may in some cases exert an effect on being introduced into the initial mixture and remain entirely ineffective after being introduced into a mixture which has already begun to react. The kinetics of nonbranched and branched chains were considered from the standpoint of N. N. Semenov's theory; it has been shown that when the chain termination effect is proportional to the first power of the concentration of active centers, the inhibitors must exert the same action on being added to the initial mixture as upon addition to a mixture which has already begun to react. Emanuel' considers that new prospects for directing chemical reactions into the desired channels are opened by the realization that the macroscopic stages follow each other in a definite sequence. (10)

On the occasion of the Conference on Chemical Kinetics, Catalysis, and Reactivity which was held in Moscow on 20-24 June 1955, Emanuel' commented as follows on current work in the field of the oxidation of hydrocarbons and the possibilities of controlling reactions of hydrocarbon oxidation and chemical reactions in general on the basis of a better knowledge of their kinetics:

"No papers on chemical kinetics as applied to combustion were presented at the conference. USSR science has to its credit great achievements in creating a theory of processes of combustion. However, at the present time the scope of work being carried out in this field is entirely insufficient. It is necessary to expand again the investigation of cold and hot flames and of processes of flame propagation and explosions.

"The principal problem of chemical kinetics is that of directing processes of chemical transformation into the desired channels. It has not been shown adequately at the conference how this can be done on the basis of a detailed knowledge of reaction mechanisms. At the same time, the suggestion has been advanced that it ought to be possible to control chemical transformations once a sufficient knowledge of macroscopic stages of complex reactions has been acquired. Macroscopic stages, which are composed of a number of elementary processes, lead to the formation of relatively stable intermediate substances of formation of final products of the reaction. As compared with the conventional way of conducting chemical reactions by establishing a set of conditions beforehand, i.e., at the very beginning of the reaction, action on the macroscopic stages which develop during the course of the reaction process is very effective.

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"Sometimes (particularly in the case of complex chain reactions) the initial period of the reaction plays a special role, so that the effects of different factors in the initial period and a later period are not the same. In many reports presented at the conference, specific chemical processes (those of oxidation, polymerization, induced chlorination in complex organic systems, etc.) were discussed from the standpoint of the concept of macroscopic stages. Expansion of research on macroscopic stages of complex chemical processes is necessary." (11)

In an investigation aiming at the clarification of the mechanism of negative catalysis in hydrocarbon oxidation, M. B. Neyman determined that no matter whether D-1-pentane, D-2-pentane, or 3-D-pentane was oxidized, formaldehyde containing deuterium was formed in every case. Experiments on the oxidation of 1- C^{14} -pentane and 3- C^{14} -pentane showed that formaldehyde is formed, not only from the end-carbons, but also from the middle carbons of the pentane chain. The results of these experiments are not in agreement with the theory of destructive oxidation: they support the assumption that oxidation of hydrocarbons proceeds in accordance with the radical-chain theory. The action of various inhibitors on the oxidation of hydrocarbons was found to take place in accordance with the equations of the chain theory. The inhibitors terminate the chains by reacting with radicals. As a result, the rate at which peroxides and aldehydes are accumulated is reduced. Unsaturated hydrocarbons, e.g., hexadiene, can be used as oxidation inhibitors. According to Neyman's results, the autocatalysis factor in oxidation drops from saturated hydrocarbons to olefins and then further to dienes. (12)

In investigating the induced autooxidation of cyclohexene to the hydroperoxide stage, B. V. Yerofeyev, A. I. Chirko, and L. N. Sorokina found that manganese stearate and cobalt stearate are effective as initiators of the reaction. Cobalt stearate proved to be the most effective initiator among those tested, while the stearates of iron and nickel and manganese formate were found to be least effective. At low concentrations of the initiator, the rate of the reaction increased with increases in the concentration of the initiator. At high concentrations such increases did not affect the rate of the reaction. To explain this relationship, Yerofeyev et al. assumed that the initiator participates both in the induction of the reaction and the termination of chains. (13)

The Effect of Oxidizing Additives on Hydrocarbon Fuels

Ye. K. Varfolomeyeva and M. V. Yerшов investigated the action of peroxide detonators (ethyl peroxide, ethyl hydroperoxide, acetone diperoxide, esters of nitric acid, and esters of nitrous acid) on the octane number and the induction period of low temperature detonation of gasolines, alcohol-gasoline mixtures, alcohol-benzene mixtures, and also of a number of individual hydrocarbons and their derivatives containing oxygen. They found that the esters of nitric and nitrous acids are stronger stimulants of detonation (knocking) than organic peroxides and that the effectiveness of their action depends on the quantity of NO contained in the molecule. The effect of peroxides on the knocking of gasolines was found to depend both on the constitution of the peroxides and the composition of the gasolines: the greatest reduction of the octane number takes place in straight-run gasolines, a smaller reduction in gasoline-benzene mixtures, and an insignificant reduction in cracking gasolines. It was noted that the action of peroxides in lowering the octane number runs parallel to that of tetraethyllead in increasing the octane number. (14)

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